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(54) Title: MIXED CHROMIUM CATALYSTS AND POLYMERIZATIONS UTILIZING SAME

(57) Abstract

Mixed catalyst compositions comprised of a first supported chromium-containing catalyst component and a second supported chromium-containing catalyst component and which additionally have one or more metallic or non-metallic catalytic agents associated therewith are provided. The additional metallic or non-metallic elements associated with the catalyst components can be aluminium, titanium, zirconium, boron, phosphorous or combinations thereof. The pore volume of the silica supports used for the first and second catalyst components differs by at least 0.3 cc/g. The mixed catalyst compositions of the invention are useful for the preparation of polyolefins. They are particularly useful of polymerization of ethylene in particle form polymerizations to produce high density polyethylene blow molding resins having good processability and physical properties. The improved particle form polymerizations process and products obtained thereby using the above-described mixed catalyst compositions are also described.

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MIXED CHROMIUM CATALYSTS  
AND POLYMERIZATIONS UTILIZING SAME

This invention relates to improved catalyst compositions and processes for utilizing same. The mixed chromium catalysts are useful for polymerizing olefins and, more particularly, for use in particle form polymerizations for the manufacture of high density polyolefin resins which exhibit high resistance to environmental stress cracking and which are useful for the production of blow molded articles. More specifically, the mixed catalysts are comprised of a first and second chromium-containing supported catalyst component wherein the supports used for said first and second catalyst components have different pore volumes and wherein at least one of the catalyst components contains an additional element selected from aluminum, titanium, zirconium, boron or phosphorus.

In the selection and production of resins for the manufacture of blow molded goods, more so than with other fabrication methods, a careful balance must be struck between the physical properties of the solid resin and the processing characteristics of the resin melt if efficient production of durable molded articles is to be achieved. While many resins have superior physical properties, they do not have acceptable rheological (viscoelastic) properties under conditions of flow and shear such as are encountered during blow molding. Conversely, other resins which exhibit satisfactory viscoelastic behavior are deficient in one or more essential physical characteristics. For this reason there is a

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1 continuing effort to develop resins which have an  
optimal balance of physical and rheological  
properties. This is especially true with polyethylene  
resins used for the manufacture of blow molded  
5 bottles.

Improved processability of polyolefin  
resins, i.e., improved flow properties and shear  
response, is obtained by increasing the molecular  
weight distribution of polymers. This has been  
10 accomplished by blending separately prepared polymers  
of different molecular weights and by utilizing  
catalyst systems capable of directly producing  
polymers having broadened molecular weight  
distributions. U.S. Patent Nos. 3,959,178 and  
15 4,025,707, for example, disclose the preparation of  
ethylene homopolymers and copolymers of broadened  
molecular weight obtained utilizing a mixed catalyst  
comprising several portions of the same or different  
chromium components and metal promoted variations  
20 thereof wherein each portion is activated at a  
different temperature. U.S. Patent Nos. 4,540,757 and  
4,560,733 utilize milled blends of at least two  
different silica-containing components having  
different melt index potentials for the preparation of  
25 titanium-containing catalysts components.

U.S. Patent No. 4,263,422 discloses  
polymerizing  $\alpha$ -olefins utilizing dual independently  
supported catalysts one of which is an inorganic  
halide supported titanium and/or vanadium Ziegler type  
30 catalyst while the other is an inorganic oxide  
supported chromium-containing catalyst.

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1 While it has been possible to improve  
processing characteristics in this manner, any  
processing advantage has heretofore been offset in  
large part by a corresponding decrease in one or more  
5 essential physical properties. For example, while the  
products obtained in accordance with U.S. Patent No.  
4,025,707 have good die swell characteristics and  
acceptable environmental stress crack resistance and  
flow properties, polymer densities are too low to  
10 provide the necessary stiffness for blown bottles. On  
the other hand, polymers such as those produced using  
the catalysts of U.S. Patent No. 4,560,733 have  
sufficiently high densities (0.960 and higher) but  
typically are deficient in their resistance to  
15 environmental stress cracking.

For blow molding bottles, the resin must  
have sufficiently high density and high resistance to  
environmental stress cracking in addition to having  
acceptable processing characteristics. A density of  
20 at least 0.957 is necessary to obtain the high degree  
of stiffness required by molders. It is considered  
even more desirable for the resin to have a density of  
0.958 to 0.961. Stiffness imparts strength to bottles  
and also makes thinner wall constructions possible.  
25 More units can thus be produced per pound of resin,  
generally referred to within the industry as  
"lightweighting", which represents an economic  
advantage for the processor. Lightweight resins must  
also exhibit a high degree of resistance to cracking  
30 under environmental stress, that is, while being  
stretched or bent in several directions at once.

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1           While stiffness increases with density as  
noted above, an inverse relationship exists between  
density and resistance to environmental stress  
cracking. As density is increased, resistance to  
5           environmental stress cracking is reduced. Both of the  
above relationships assume that the melt index of the  
resins are the same or essentially the same. A  
balance must therefore be struck between the density,  
i.e., stiffness, of the resin and the resistance of  
10          the resin to environmental stress cracking.

          It would be advantageous if the molecular  
weight distribution of polymers would be varied and if  
polyethylene resins having an optimal balance of  
rheological and physical properties could be produced.  
15          It would be even more desirable if high density resins  
having high resistance to stress cracking useful for  
the manufacture of blown bottles could be obtained  
utilizing mixtures of known catalyst components.  
These and other advantages are realized using the  
20          mixed catalyst compositions of the present invention  
which are described in detail to follow.

          The present invention relates to a mixed  
chromium catalyst composition containing a first and  
second silica-supported chromium catalyst component;  
25          said first and second catalyst components present at a  
weight ratio from 10:1 to 1:10 and each containing  
from 0.1 to 2.0 weight percent chromium with at least  
one of said catalyst components containing an  
additional metallic or non-metallic element selected  
30          from aluminum, titanium, zirconium, boron or  
phosphorus with the proviso that when one of the  
catalytic components contains chromium and aluminum

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1 the other component shall contain more than one  
metallic or non-metallic catalytic element; and the  
silica supports of said first and second catalyst  
components differing in pore volume by at least 0.3  
5 cc/g. The mixed chromium catalyst compositions of the  
present invention consist essentially of a first and  
second silica-supported chromium catalyst component;  
said first and second catalyst components present at a  
weight ratio from 10:1 to 1:10 and each containing  
10 from 0.1 to 2.0 weight percent chromium with at least  
one of said catalyst components containing an  
additional metallic or non-metallic element selected  
from aluminum, titanium, zirconium, boron or  
phosphorus. The silica supports of said first and  
15 second catalyst components differ in pore volume by at  
least 0.3 cc/g and, most usually, the pore volume of  
the silica support of the first catalyst component is  
greater than 1.0 cc/g.

In a particularly useful embodiment of the  
20 invention the pore volume of the silica support used  
for the first catalyst component is from 1.7 to 3.1  
cc/g and the pore volume of the silica support used  
for the second catalyst component is from 1.0 to 2.0  
cc/g. The weight ratio of the first and second  
25 catalyst components will more preferably range from  
5:1 to 1:5 and the metallic and non-metallic  
element(s) are usually present in amounts from 0.1 to  
6.0 weight percent. Especially useful mixed catalysts  
of the invention contain from 2 to 4.5 weight percent  
30 aluminum, titanium, or zirconium and, when a non-metal  
is present, from 0.1 to 1.0 weight percent phosphorous  
or boron.

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1           In another particularly advantageous  
embodiment, the individual catalyst components or a  
mixture of the catalyst components are thermally  
activated by heating in a non-reducing atmosphere at a  
5   temperature from 450°F to 1700°F. It is even more  
useful if, prior to the thermal activation, the  
individual catalyst component or mixture thereof is  
heated at 575°F to 1650°F in a reducing atmosphere -  
preferably a mixture of nitrogen and carbon monoxide.  
10   The mixed chromium compositions are effective  
catalysts for the polymerization of olefins by  
themselves or, as is more generally the case, in  
combination with metallic or non-metallic reducing  
agents such as trialkyl aluminums, alkyl aluminum  
15   halides, alkyl aluminum alkoxides, dialkyl zincs,  
dialkyl magnesiums, alkali metal borohydrides,  
aluminum borohydrides, alkyl boranes, and boron  
hydrides.

          In accordance with the present invention,  
20   polyethylene resins having good processing  
characteristics, high density and high resistance to  
environmental stress cracking are obtained using mixed  
chromium catalysts obtained by combining two or more  
different supported chromium-containing catalyst  
25   components. The catalyst components which are mixed  
to obtain the present catalyst compositions will  
differ based on the support material used and may also  
differ based on the type and/or amount of catalytic  
agent associated therewith. Whereas the individual  
30   chromium-containing catalyst components may be known,  
it has unexpectedly been discovered that by combining  
certain of these catalyst components in specific

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1 ratios the resulting mixed catalysts yield resins  
which, in addition to having excellent processing  
characteristics by virtue of a broadened molecular  
weight distribution, also have high densities and high  
5 resistance to environmental stress cracking. This  
balance of desirable processability with both high  
density and high resistance to stress cracking makes  
the resins highly useful in blow molding applications  
and particularly for the production of blown bottles.

10 Polyethylene resins having densities of at  
least 0.957, high environmental stress cracking  
resistance (ESCR), and acceptable flow properties and  
shear response are obtained using the present improved  
catalyst compositions which are mixtures of first and  
15 second chromium-containing silica supported catalyst  
components wherein the silica supports for said  
catalyst components differ in pore volumes by at least  
0.3 cc/g and at least one of the catalyst components  
contains an additional metallic or nonmetallic element  
20 selected from aluminum, titanium, zirconium, boron or  
phosphorus. These catalytic metallic and nonmetallic  
elements, also referred to herein as catalytic agents,  
will be deposited on and associated with the support  
material in accordance with conventional practice.  
25 More particularly, resins produced in accordance with  
the present invention have densities from 0.958 to  
0.961 and ESCR values greater than 8 hours and, more  
preferably, greater than 10 hours. ESCR values  
referred to herein are bottle ESCR F50 values as  
30 determined in accordance with ASTM D-2561, Procedure C  
(modified), unless otherwise indicated.

35

1           In addition to having densities and bottle  
ESCRs within the above-specified ranges, the resins  
also typically have melt indexes (pellet) from 0.1 to  
0.7 and, more particularly, in the range 0.2 to 0.4  
5           and melt index ratios (MIRs) in the range 60 to 180  
and, more preferably, 80 to 125. MIR is generally  
considered to be an approximation of molecular weight  
distribution and is the ratio between the high load  
melt index (HLMI) determined in accordance with ASTM  
10          D1238-57T, condition F, and the MI determined in  
accordance with ASTM D1238-57T, condition E. In  
general, with resins of comparable MI, polymers with  
broader molecular weight distributions have higher  
MIRs and better flow properties than their lower MIR  
15          counterparts.

          While it is generally recognized that  
rheological properties can be modified by varying the  
support material used for a particular catalyst and  
that the melt index is affected by the pore volume of  
20          the silica support, it is unexpected the above-  
described highly desirable balance of rheological and  
physical properties can be obtained by the use of  
mixed catalysts based on two different chromium-  
containing components. Heretofore, any processing  
25          advantages which have been realized were generally  
accompanied by a corresponding undesirable reduction  
in density and/or ESCR.

          The catalyst compositions of the present  
invention are mixtures of two discreet supported  
30          catalyst components present in defined ratios. Both  
catalyst components employed for the improved mixed  
catalyst compositions of the invention necessarily

1        have chromium on a support. Additionally, one or both  
of the catalyst components may also have other  
metals/nonmetals deposited thereon.

5        Silica is utilized as the support for the  
two catalyst components, however, the silica employed  
for the first catalyst component and the silica used  
for the second catalyst component will differ in pore  
volumes by at least 0.3 cc/g. The weight ratio of the  
first and second supported catalyst component in the  
10       mixture ranges from 10:1 to 1:10 and, more preferably,  
from 5:1 to 1:5. In a particularly useful embodiment  
the weight ratio of the two catalyst components  
comprising the mixture is from 3:1 to 1:3.

15       The silica support employed for the first  
catalyst, referred to herein as the higher pore volume  
support, will have a pore volume greater than 1.0  
cc/g. This higher pore volume support more usually  
has a pore volume of 1.7 cc/g or above and in a  
particularly useful embodiment the pore volume is  
20       greater than 2.0 cc/g. In general, the pore volume  
will not exceed about 3.1 cc/g. Silica supports of  
this type are well known and can be obtained in  
accordance with known procedures. For example, silica  
xerogels having the prescribed pore volumes are  
25       described in U.S. Patent Nos. 3,652,214, 3,652,215 and  
3,652,216, details of which are incorporated herein by  
reference.

30       Especially useful high pore volume silicas  
for the catalysts of this invention have pore volumes  
from 2.1 cc/g to 2.9 cc/g. These high pore volume  
materials typically have surface areas in the range

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1 100 to 800 m<sup>2</sup>/g and, more preferably, in the range 200  
to 500 m<sup>2</sup>/g.

5 The silica support employed for the second  
catalyst component, referred to herein as the lower  
pore volume support, will have a pore volume at least  
0.3 cc/g less than the higher pore volume support  
employed for the first catalyst component. In  
general, the pore volume of these silicas can range  
10 from 0.3 to 2.6 cc/g but, more usually, will range  
from 1.0 to 2.0 cc/g. It is particularly advantageous  
if the second catalyst component is supported on a  
silica support having a pore volume from 1.5 cc/g to  
1.9 cc/g.

15 While granular silica supports are most  
commonly used, microspheroidal silicas can be  
advantageously utilized as the support material for  
either or both catalyst components. Silica xerogels  
of this later type are obtained by conventional  
methods known to the art such as described in U.S.  
20 Patent No. 3,453,077, and are commercially available  
from Davison Chemical Division, W.R. Grace & Co.,  
under the designation MS-952. Microspheroidal silica  
of pore volume 1.6 cc/g to 1.8 cc/g is most  
advantageously employed as the lower pore volume  
25 support for the second catalyst component.

30 Either or both of the silica supports can be  
calcined prior to having the metal deposited thereon.  
If calcining is employed prior to deposition, it can  
be carried out at temperatures ranging from about  
200°F to about 1800°F in accordance with conventional  
procedures. In one particularly useful embodiment of  
the invention the higher pore volume silica support

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1        used for the first catalyst component is calcined  
before deposition.

5                Known chromium-containing compounds capable  
of reacting with the surface hydroxyl groups of the  
silica supports can be utilized to effect deposition  
of the chromium thereon. Examples of such compounds  
include chromium nitrate, chromium trioxide,  
10        organochromium compounds, including chromocene,  
chromate esters such as chromium acetate, chromium  
acetylacetonate and t-butyl chromate, silyl chromate  
esters, phosphorus-containing chromate esters, and the  
like.

15                When an additional catalytic agent, metal or  
nonmetal, is present on either the first or the second  
catalyst component it can be deposited in the  
conventional manner. For example, a compound of the  
metal or nonmetal can be included with the chromium  
compound during the chromium deposition or, after the  
chromium deposition is complete, any additional  
20        catalytic agents can be deposited in a separate step.  
It is also possible to utilize a chromium compound or  
complex containing additional catalytic elements.  
This latter procedure is especially useful where  
phosphorus or boron are to be deposited on either the  
25        first or second catalyst component. Most notable in  
this regard is the use of organophosphoryl chromium  
compounds of the type disclosed in U.S. Patent No.  
3,985,676.

30                Known aluminum-containing compounds capable  
of reacting with the surface hydroxyl group of the  
silica supports can be employed to deposit the  
aluminum thereon. Examples of such aluminum compounds

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1 include aluminum alkoxides, such as aluminum sec-  
butoxide, aluminum ethoxide, aluminum isopropoxide;  
alkyl aluminum alkoxides, such as ethyl aluminum  
ethoxide, methyl aluminum propoxide, diethyl aluminum  
5 ethoxide, diisobutyl aluminum ethoxide, etc.; alkyl  
aluminum compounds, such as triethyl aluminum,  
triisobutyl aluminum, etc.; alkyl or aryl aluminum  
halides, such as diethyl aluminum chloride; aryl  
aluminum compounds, such as triphenyl aluminum;  
10 aryloxy aluminum compounds, such as aluminum  
phenoxide; and the like. While the aluminum may be  
deposited on either the first or second component of  
the mixed catalyst, it is preferably associated with  
the first catalyst component and supported on the high  
15 pore volume silica.

Compounds which can be utilized to  
incorporate titanium and zirconium metal with the  
support include titanates and zirconates of the  
formula



20 where Me is titanium or zirconium; R is a hydrocarbon  
radical selected from alkyl, cycloalkyl, aryl, aralkyl  
or alkaryl having from 1-12 carbon atoms; m is an  
integer from 1 to 4, n is an integer from 0 to 3 and m  
plus n is equal to 4; and titanium or zirconium  
25 halides of the formula



where Me is titanium or zirconium and X is chlorine,  
bromine, fluorine or iodine. Compounds of the above  
types wherein R is a  $C_{1-7}$  alkyl group and X is  
30 chlorine are particularly useful. In an even more

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1        advantageous embodiment of the invention the titanium  
          and zirconium compounds are represented by the formula

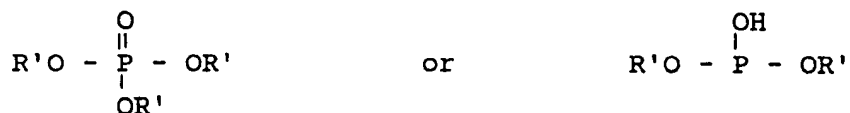


         where Me is the same as defined above and  $\text{R}_1$  is a  $\text{C}_{1-7}$   
 5        alkyl group, for example, tetraethyl titanate,  
          tetraisopropyl titanate, tetraisopropyl zirconate,  
          tetrabutyl titanate, etc. These latter compounds,  
          also sometimes referred to as titanium tetraethoxide,  
          titanium tetraisopropoxide, zirconium  
 10       tetraisopropoxide and titanium tetrabutoxide,  
          respectively, are conveniently deposited on support  
          materials by deposition from hydrocarbon solutions.  
          Tetraisopropyl titanate and tetraisopropyl  
          zirconate are especially preferred.

15       Titanium and zirconium acetylacetonate  
          compounds, such as titanyl acetylacetonate and  
          titanium diacetylacetonate diisopropylate, can also be  
          used to deposit these metals.

         Boron is conveniently deposited utilizing an  
 20       alkyl ester of boron wherein the alkyl group contains  
          from 1 to 7 carbon atoms, such as trimethyl borate and  
          triisopropyl borate, or a halide of boron.

         Phosphorus compounds which can be used to  
          effect deposition are most commonly phosphate esters  
 25       which correspond to the formulas



         where R is a hydrocarbon radical selected from alkyl,  
 30       cycloalkyl, aryl, aralkyl and alkaryl having from 1 to  
          12 carbon atoms. Trialkyl phosphates where the alkyl

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1 group contains from 1 to 7 carbon atoms, such as  
triethyl phosphate, are particularly useful.

5 The first and second components which  
comprise the mixed catalysts of the invention are  
obtained by depositing the chromium-containing  
compound and any additional catalytic agents on the  
silica support in accordance with conventional known  
procedures, e.g., vapor coating or deposition from  
inert organic solvents. Organic solvents which can be  
10 employed for this purpose typically include  
hydrocarbons and their halogenated derivatives.  
Dichloromethane has been found to be a particularly  
effective solvent for depositing chromium and aluminum  
compounds on the supports.

15 The same or different chromium-containing  
compounds may be used for preparation of the first and  
second catalyst components. When preparing catalyst  
components having chromium and one or more other  
elements the order of deposition may be varied where  
20 separate steps are employed. Furthermore, after the  
first deposition the support having the metal  
deposited thereon may be heat activated before  
proceeding with subsequent depositions.

25 In general, the first and second catalyst  
components can contain from about 0.1 to 2.0 weight  
percent chromium. More usually, however, the amount  
of chromium will range from 0.2 to 1.5 weight percent  
and in a particularly useful embodiment from 0.5 to  
1.25 weight percent. Additional metal and nonmetal  
30 catalytic agents will be present from 0.1 to 6.0  
weight percent and, more preferably, from 0.2 to 4.0  
weight percent.

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1 More specifically, when a metallic catalytic  
agent is employed in conjunction with the chromium,  
such as when titanium, zirconium or aluminum are  
present, these metals will constitute from 0.5 to 6.0  
5 weight percent and, more preferably, 1.0 to 4.0 weight  
percent of the catalyst component. Nonmetallic  
cocatalytic agents, when present on either the first  
or second catalyst component, will generally range  
from 0.1 to 1.5 weight percent and, more usually, from  
10 0.2 to 1.0 weight percent. In a highly useful  
embodiment of the invention, the first catalyst  
component contains from 0.5 to 1.2 weight percent  
chromium, the second catalyst component contains from  
0.75 to 1.25 weight percent chromium, and aluminum is  
15 associated with the first higher pore volume catalyst  
component and is present in an amount from 2 to 4.5  
weight percent. In all of the foregoing instances,  
the recited weight percentages are based on the total  
weight of the catalyst component.

20 The first and second catalyst components  
comprising the mixed catalyst compositions of this  
invention are thermally activated by heating at a  
temperature below the decomposition temperature of the  
support material in a non-reducing atmosphere. The  
25 heat activation may be carried out before the first  
and second catalyst components are combined or after  
the first and second catalyst components have been  
combined. Temperatures generally employed for this  
activation range from about 450°F up to about 1700°F  
30 but higher activation temperatures can be utilized  
provided the decomposition temperature of the support  
material is not exceeded. When the first and second

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1 catalyst components are combined and co-activated by  
heating the mixture of the catalyst, temperatures from  
about 950°F to 1500°F are preferably used. When the  
first and second catalyst components are separately  
5 heat activated, temperatures from 950°F to 1650°F are  
most advantageously employed. In the latter  
situation, the catalyst components may be heat  
activated at different temperatures within the above-  
recited range. Also, multiple heat activation steps  
10 may be carried out. For example, after the first  
compound is deposited on the support and before  
proceeding with deposition of the second a heat  
activation operation may be carried out. Similarly,  
after deposition of the second compound, a second heat  
15 activation operation may be conducted or the catalytic  
material may be directly combined with the other  
catalyst component and this mixture then heat  
activated.

A non-reducing atmosphere, preferably, an  
20 oxygen-containing atmosphere is necessarily employed  
for thermal activation. The time required will vary  
but generally ranges from about 30 minutes up to about  
24 hours and, more preferably, from 2 to 12 hours. If  
the first and second catalyst components are  
25 separately heat activated, the temperatures employed  
and times of activation may be different for each.  
The non-reducing atmosphere, which is preferably air  
or other oxygen-containing gas, should be essentially  
dry. When air is used, it is preferably dehumidified  
30 to less than 3 ppm water.

In a particularly useful embodiment of this  
invention, the thermal activation is preceded by

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1 heating the individual catalyst components or the  
mixed catalyst composition at a temperature from about  
575°F to 1650°F in a reducing atmosphere for a period  
of time which can range from several minutes up to  
5 several hours. Preferably the reducing atmosphere  
consists of a mixture of an inert gas with a reducing  
gas. Such procedures are described in U.S. Patent No.  
4,041,224. Preferably, the inert gas is nitrogen and  
the reducing gas is carbon monoxide and the  
10 temperature is between about 1000°F and 1400°F.  
Following this reductive treatment step, the catalyst  
is then subjected to thermal treatment in the non-  
reducing gas in accordance with the previously  
described procedure. Where a reducing step is  
15 employed prior to activation in a non-reducing  
atmosphere, the latter step is preferably carried out  
at a temperature from about 800°F to 1100°F.

The mixed catalysts of the invention are  
effective to polymerize olefins by themselves or in  
20 combination with metallic and/or non-metallic reducing  
agents. Examples of metallic reducing agents which  
can be used include trialkyl aluminums, such as  
triethyl aluminum and triisobutyl aluminum, alkyl  
aluminum halides, alkyl aluminum alkoxides, dialkyl  
25 zincs, dialkyl magnesiums, and borohydrides including  
those of the alkali metals, especially sodium, lithium  
and potassium, and aluminum. Non-metal reducing  
agents which can be used include alkyl boranes such as  
triethyl borane, triisobutyl borane, and trimethyl  
30 borane and hydrides of boron such as diborane,  
pentaborane, hexaborane and decaborane. The mixed  
catalyst may be combined with the metallic or non-

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1 metallic reducing agent prior to being fed to the  
polymerization vessel or the mixed catalyst and  
reducing agent may be separately fed to the  
polymerization reactor. The molar ratio of the metal  
5 or non-metal of the reducing agent to chromium can  
range from 0.01:1 to 10:1 and more preferably, is in  
the range 0.01:1 to 5:1. In a particularly  
advantageous embodiment, the molar ratio of metal or  
non-metal to chromium is from 0.01:1 to 2:1.

10 In one embodiment of the invention  
particularly useful polyethylene resins having a good  
balance of physical and rheological properties useful  
for the manufacture of blow molded bottles are  
produced utilizing a mixed catalyst composition  
15 wherein the first catalyst component contains from 0.5  
to 1.2 weight percent chromium and from 0.2 to 1.0  
weight phosphorus obtained by depositing an  
organophosphoryl chromium compound and 2 to 4.5 weight  
percent aluminum obtained by depositing an aluminum  
20 alkoxide compound, said compounds being deposited on a  
silica support having a pore volume from 2.1 cc/g to  
2.9 cc/g. It is especially advantageous if the high  
pore volume silica support is calcined at 1200°F to  
1700°F prior to deposition of the chromium and  
25 aluminum compounds.

Chromium/aluminum-containing catalysts of  
this type are known and described in U.S. Patent No.  
3,984,351, details of which are incorporated herein by  
reference. In general, they are obtained by  
30 depositing an organophosphoryl chromium compound which  
is the reaction product of chromium trioxide and an  
organophosphorus compound of the formula

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5 wherein at least one of the R' groups is a hydrocarbon radical selected from alkyl, cycloalkyl aryl, aralkyl, or alkaryl. Any R' groups which are not hydrocarbon radicals are hydrogen. Preferred organophosphorus compounds are trialkyl phosphates such as triethyl phosphate. The aluminum alkoxide compounds correspond to the formula



15 where R'' is an alkyl having from 1 to 8 carbon atoms or aryl, aralkyl, or alkaryl having from 6 to 8 carbon atoms. Aluminum sec-butoxide, aluminum isopropoxide, aluminum ethoxide, and aluminum phenoxide are representative aluminum alkoxides and aluminum sec-butoxide is particularly advantageous.

Especially advantageous results are obtained when the above-described first catalyst component is used in conjunction with a second catalyst component containing from 0.75 to 1.25 weight percent chromium obtained by depositing a chromate ester on a microspheroidal silica support having a pore volume from 1.6 cc/g to 1.8 cc/g. Chromium acetate is a particularly useful chromate ester. Synthetic microspheroidal (amorphous) silica xerogels impregnated with chromium acetate are commercially available, e.g., EP30 Polyolefin Catalyst from Crosfield Catalysts. It is even more desirable if a trialkyl borane reducing agent is included in the polymerization with the above-described components and

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1 when the molar ratio of the boron of the reducing  
agent to chromium ranges from 0.1:1 to 1.5:1.

5 In another highly useful embodiment the  
above-described higher pore volume catalyst component  
contains chromium and titanium and, optionally,  
phosphorus. These catalyst components are effective  
when employed in conjunction with the above-described  
10 second catalyst components obtained by depositing  
chromium acetate on microspheroidal silica but are  
particularly advantageous when used with a catalyst  
component based on the lower pore volume support and  
having titanium or zirconium deposited with the  
chromium. In an even further and more preferred  
15 embodiment, mixed catalyst compositions which contain  
zirconium or titanium by virtue of having these metals  
deposited with the chromium on either the first or  
second catalyst component are thermally activated  
utilizing the two step procedure wherein the catalyst  
20 is first heated in a reducing atmosphere of carbon  
monoxide and subsequently in a non-reducing atmosphere  
of air. When zirconium and/or titanium are employed  
they are generally present from about 2 to 4 weight  
percent and if phosphorous is employed it generally is  
present from about 0.1 to 1.0 weight percent.

25 While the catalyst compositions of the  
present invention find general utility for the  
polymerization of olefins to produce homopolymers and  
copolymers in the density range 9.10 to about 9.70,  
they are most advantageously employed for the  
30 preparation of ethylene homo- and copolymer resins  
which have a desirable balance of rheological and  
physical properties making them useful for blow

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1       molding applications. Resins produced in accordance  
with the invention are primarily used for blow molding  
bottles, especially detergent bottles, bleach bottles  
and milk bottles, but can also be used for the  
5       production of larger articles such as blowmolded drums  
and tanks. Resins obtained using the present improved  
mixed catalyst compositions are also useful for films.  
For example, high molecular weight film resins  
suitable for grocery sacks and merchandise bags and  
10       medium molecular weight resins for use in cereal  
liners and snack packs can also be produced using the  
mixed catalysts of the invention.

Utilizing the above-described preferred  
mixed catalysts, it is possible to produce highly  
15       processable, high density polyethylene resins which  
have high resistance to environmental stress cracking.  
For example, polyethylene resins having densities in  
the range 0.958 to 0.961 and ESCRs greater than 10  
hours with melt indexes in the blowmolding range of  
20       0.1 to 0.7 and melt index ratios from 80 to 125 are  
readily produced. By judicious selection of the  
various catalyst parameters discussed above it is  
possible to produce resins having acceptable stiffness  
with melt indexes from 0.2 to 0.4 and to achieve even  
25       further broadening of the molecular weight  
distribution, i.e., higher MIRs. In some instances  
the production of bimodal resins is even possible. It  
is an especially desirable feature of this invention  
that these aforementioned highly useful polyethylene  
30       resin products can be obtained using mixed catalysts  
without the necessity of separately heat activating  
the first and second catalyst components. This

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1 feature is an extremely useful and beneficial aspect  
of the invention from a commercial point of view since  
it eliminates a step in the catalyst preparation.

5 The mixed catalyst compositions can be used  
in virtually any polymerization procedure where  
supported catalysts are utilized. This includes both  
gas phase (fixed and fluidized bed) polymerizations  
and solution polymerizations. They are, however,  
10 primarily used for the polymerization of ethylene in  
conventional particle form (slurry) processes. Such  
procedures are well known and are described in the  
prior art, e.g., U.S. Patent No. 3,644,323. In  
general these polymerizations are carried out in a  
15 liquid organic medium at a temperature from about  
150°F to 230°F. The catalyst is suspended in the  
organic medium and the reaction is conducted at a  
pressure sufficient to maintain the organic diluent  
and at least a portion of the olefin in the liquid  
phase. Weight percent ethylene in the reactor is  
20 generally maintained from about 1.5 up to about 7.  
Hydrogen is generally added to the polymerization  
reaction for molecular weight control. The molar  
ratio of hydrogen to ethylene in the reactor is  
generally maintained between 0.25 and 1.0. While not  
25 necessary for polymerization, a metallic or non-  
metallic reducing agent of the type previously defined  
is generally included in polymerizations with the  
mixed catalysts of this invention.

30 The organic medium employed for the  
polymerization is generally a paraffinic and/or  
cycloparaffinic material such as propane, butane,  
isobutane, pentane, isopentane, cyclohexane,

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1 methylcyclohexane, and the like. The medium is chosen  
so that under the conditions employed the polymer is  
insoluble in the medium and is readily recoverable in  
the form of solid particles. Isobutane is a  
5 particularly advantageous organic medium for the  
purpose of these polymerizations. Pressures typically  
range from about 100 to 800 psig and catalyst  
concentrations can range from about 0.001 to about 1  
percent, based on the total weight of the reactor  
10 contents. These slurry polymerizations can be  
conducted as batch, continuous or semi-continuous  
operations.

The following examples illustrate the  
invention more fully. They demonstrate the ability to  
15 produce a wide range of readily processable  
polyethylene resins having high densities and high  
resistance to environmental stress cracking. Unless  
otherwise indicated, all parts and percentages are on  
a weight basis.

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EXAMPLE I

1 A mixed catalyst was prepared in accordance  
with the present invention and utilized for the  
polymerization of ethylene. The catalyst consisted of  
5 a mixture of a supported chromium/aluminum catalyst  
prepared in accordance with the procedure of U.S.  
Patent No. 3,984,351, identified as Catalyst Component  
A, and a supported chromium catalyst obtained from  
commercial sources, identified as Catalyst Component  
10 B.

Catalyst Component A was prepared by  
calcining a high pore volume silica support at 1650°F  
for 6 hours and thereafter impregnating first with the  
reaction product of CrO<sub>3</sub> and triethyl phosphate and  
15 then with aluminum sec-butoxide. Impregnations were  
made by deposition from dichloromethane solutions.  
The impregnated catalyst was then activated by placing  
it in a cylindrical container and fluidizing with dry  
air at 0.2 feet per minute lineal velocity while  
20 heating at 1070°F for 6 hours. The resulting heat-  
activated catalyst had a pore volume of 2.3 cc/g and  
contained 1.0% chromium, 3.7% aluminum, and 0.6%  
phosphorus.

Catalyst Component B was a commercially  
25 obtained microspheroidal silica xerogel impregnated  
with chromium acetate which was activated by  
fluidizing with dry air at 0.2 feet per minute lineal  
velocity and heating at 1000°F for 6 hours. The  
resulting heat-activated chromium catalyst had a pore  
30 volume of 1.7 cc/g and contained 1.0% chromium.  
Catalyst Components A and B were blended at a weight  
ratio of 3:1 to obtain the mixed catalyst.

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1 Polymerization was carried out in a jacketed  
loop-type reactor provided with an agitator to cause  
circulation within the loop and create highly  
turbulent flow. Isobutane was employed as the  
5 hydrocarbon reaction medium. Means were provided to  
continuously feed isobutane, ethylene, a slurry of the  
mixed catalyst in isobutane, a solution of triethyl  
boron in isobutane and hydrogen to the reactor and for  
removing a mixture of the polymer, unreacted monomer,  
10 and diluent at a controlled rate. Polymerization  
details were as follows:

Temperature (°F)	213
Catalyst Concentration (g/kg isobutane)	0.38
Ethylene in Reactor (%)	3.19
15 H <sub>2</sub> /Ethylene Molar Ratio	0.49
Boron/Chromium Molar Ratio	0.24

After removal of ethylene and isobutane a  
free-flowing polyethylene powder having a density of  
0.9599 and ESCR of 10.1 hours per ASTM D-2561,  
20 Procedure C was obtained. The resin had an MI of 0.26  
and MIR of 119 and was readily fabricated using  
conventional blowmolding equipment into blown bottles.

The above polymerization was repeated except  
that the conditions were varied as follows:

25 Temperature (°F)	212
Catalyst Concentration (g/kg isobutane)	0.40
Ethylene in Reactor (%)	2.97
H <sub>2</sub> /Ethylene Molar Ratio	0.49
Boron/Chromium Molar Ratio	0.25

30 The resulting polyethylene resin had a density of  
0.9595, ESCR of 10.5 hours, MI 0.20, and MIR of 122.

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1           A useful high density resin was obtained  
even when the mixed catalyst was employed without  
triethyl borane reducing agent. For example, when  
5           ethylene was polymerized at 214°F using a catalyst  
concentration of 0.73 g/kg isobutane with 3.81 weight  
percent ethylene and H<sub>2</sub>/ethylene molar ratio of 0.35,  
a resin having a density of 0.9601, ESCR of 8.9 hours,  
10          MI of 0.26, and MIR of 130 was obtained. While the  
environmental stress crack resistance of the resin was  
somewhat lower than that obtained when triethyl borane  
is used, it nevertheless is considered to be within  
acceptable limits.

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EXAMPLE II

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To further demonstrate the ability to obtain high density resins having increased environmental stress crack resistance, a mixed catalyst was prepared by blending Catalyst Components A and B of Example I at a weight ratio of 1:1. The catalyst was employed for the polymerization of ethylene in accordance with the procedure of Example I under the following conditions:

10

Temperature (°F)	212
Catalyst Concentration (g/kg isobutane)	0.41
Ethylene in Reactor (%)	2.17
Hydrogen/Ethylene Molar Ratio	0.89

15

The resulting polyethylene resin had a density of 0.9601 and ESCR of 11.4 hours. The MI and MIR of the resin were 0.26 and 110, respectively.

20

When the polymerization was repeated increasing the ethylene in the reactor to 2.82% and lowering the hydrogen/ethylene molar ratio to 0.69, a resin of density 0.9606, ESCR of 10.1 hours, MI of 0.24, and MIR of 118 was obtained.

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EXAMPLE III

A chromium/aluminum/phosphorus catalyst, identified as Catalyst Component C, was prepared as described for Catalyst Component A in Example I except that the high pore volume silica support was not calcined prior to deposition of the chromium and aluminum compounds. After deposition of the chromium and aluminum compounds, Component C was air-dried and combined at a 1:1 weight ratio with a commercial chromium acetate impregnated microspheroidal silica xerogel (1.0% Cr; pore volume 1.7 cc/g). The mixture was then co-activated by fluidizing the mixture with dry air at 0.2 feet per minute lineal velocity and heating at 1100°F for 6 hours. The resulting heat-activated mixed catalyst was employed for the polymerization of ethylene. Polymerization conditions and properties of the resulting resin-produced thereby were as follows:

	Temperature (°F)	218
20	Catalyst Concentration (g/kg isobutane)	0.40
	Ethylene in Reactor (%)	4.0
	H <sub>2</sub> /Ethylene Molar Ratio	0.28
	Boron/Chromium Molar Ratio	0.14
	Density	0.9592
25	ESCR (hours)	12
	MI	0.23
	MIR	113

It is evident from the foregoing data that the product produced in accordance with the above-defined polymerization conditions has an excellent balance of physical and rheological properties which make it useful for blow molding applications. when

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1     the above-defined catalyst components are individually  
employed for the polymerization of ethylene under  
comparable polymerization conditions, resins having  
the desired balance of physical and rheological  
5     properties are not produced. For example, when high  
density resins having acceptable rheological  
properties are obtained, the stress crack resistance  
of the polymers is deficient.

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EXAMPLE IV

1 To demonstrate the significant improvement  
obtained with the mixed catalyst compositions of this  
invention, polyethylene resin produced using a mixed  
5 catalyst was compared with resins produced using the  
individual catalyst components.

A supported catalyst containing chromium,  
aluminum and phosphorus was prepared in accordance  
with the general procedure described for Catalyst  
10 Component A in Example I using a high pore volume  
silica support (2.24 cc/g). The high pore volume  
silica was dried at 550°F for two hours prior to  
deposition and then impregnated first with the  
reaction product of  $\text{CrO}_3$  and triethyl phosphate and  
15 then with aluminum sec-butoxide. The depositions were  
made from dichloromethane solutions in accordance with  
the procedure described in U.S. Patent No. 3,984,351.  
After drying the resulting supported catalyst  
(identified as IV(a)) had the following analysis:  
20 0.90% Chromium; 3.70% Aluminum; and 0.54% phosphorus.

A supported catalyst containing chromium on  
a lower pore volume silica and corresponding to  
catalyst component B in Example I was employed as the  
second catalyst component and identified as IV(b).  
25 The catalyst was a commercially available  
microspheroidal silica xerogel impregnated with  
chromium acetate (1.0% Cr) purchased from Davison  
Chemical Division, W.R. Grace & Co. under the  
designation MS-952.

30 To obtain the mixed catalyst components  
IV(a) and IV(b) were combined in equal weight  
proportions and blended by fluidizing with dry air at

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1     0.2 feet per minute lineal velocity. The resulting  
mixed catalyst, identified as IV(mc), was not analyzed  
since the metal values and pore volume are one-half of  
the sum of the values of the individual catalyst  
5     components.

Each of the above catalysts IV(a), IV(b),  
and IV(mc), was used to polymerize ethylene in the  
particle form polymerization process. Prior to  
polymerization each catalyst was heat-activated in a  
10     non-reducing atmosphere in accordance with the general  
practice, i.e., by fluidizing with dry air at 0.2 feet  
per minute lineal velocity and heating for a specified  
time. Conditions employed for the heat activation and  
polymerization with each of the above catalysts were  
15     selected to produce polyethylene resins suitable for  
blow molding having comparable densities (greater than  
0.957) and comparable MIs (in the preferred range of  
0.1 to 0.4). Polymerizations were then carried out in  
a production-scale jacketed loop reactor which was  
20     highly agitated to create circular highly turbulent  
flow within the loop. Isobutane was employed as the  
hydrocarbon reaction medium and, in accordance with  
the preferred practice for this type of  
polymerization, a co-catalyst (triethyl borane) and  
25     modifier (hydrogen) were employed. Heat activation  
details, polymerization details and properties of the  
polyethylene resins produced with each catalyst were  
as follows:

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1		CATALYST IV(a)	CATALYST IV(b)	CATALYST IV(mc)
	Heat Activation:			
5	Temp. (°F)	1200	1600 <sup>1</sup>	1100
	Time (hours)	6	6	6
	Polymerization:			
10	Temp. (°F)	214	224	220
	Press (psig)	650	650	650
	Catalyst Conc. (g/kg isobutane)	0.40	0.38	0.19
15	C <sub>2</sub> H <sub>4</sub> in Reactor (wt.%)	3.2	3.5	4.45
	H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> Molar Ratio	0.36	0.08	0.28
	B/Cr Molar Ratio	0.19	0.42	0.27
20	% Solids	41	39	38.5
	Polyethylene Resin:			
	Density	0.9595	0.9596	0.9592
	MI (pellet)	0.36	0.34	0.28
25	MIR	95.5	98.5	107.7

<sup>1</sup>High activation temperature is required with this catalyst to produce a resin with MI in the desired range.

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1                   Standard blow molded containers (shampoo  
bottles) were produced using each of the above-  
identified resins and evaluated for environmental  
stress crack resistance in accordance with modified  
5   ASTM D-2561, Procedure C, Controlled Elevated Pressure  
Stress-Crack Resistance of a Specific Container to  
Polyoxyethylated Nonylphenol, a Stress-Cracking Agent.  
In this test the internal pressure is controlled at a  
constant elevated level. The shampoo bottles blow  
10   molded from the resins produced using Catalysts IV(a)  
and IV(b) failed after 8.5 and 10.5 hours,  
respectively, whereas the bottles formed from the  
resin produced using mixed catalyst IV(mc) ran for  
19.8 hours before failure.

15                   Blown containers produced using the above-  
identified polyethylene resins were also evaluated for  
column crush properties in accordance with ASTM D  
2659-84. This test determines the mechanical  
properties of blown thermoplastic containers when  
20   loaded under columnar crush conditions at a constant  
rate of compressive deflection. For this evaluation  
the specimens tested were bleach bottles blow molded  
using  $25 \pm 0.10$  grams of the resin. Results were as  
follows:

25

Resin Produced Using	<u>CATALYST IV(a)</u>	<u>CATALYST IV(b)</u>	<u>CATALYST IV(mc)</u>
Crushing Load at Failure (lbs)	57.5	57.2	63.2

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It is apparent from the above data that the  
increased column crush value obtained with the resin  
produced using the mixed catalyst IV(mc) would make it

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1 possible to lightweight the bleach bottles by 10 to 15  
percent.

5 To further demonstrate the versatility of  
the invention and the ability to vary the catalyst  
components, a series of experiments were conducted  
using different mixed catalysts and are reported in  
the examples which follow. Catalyst components used  
to prepare the mixed catalysts referred to in Examples  
V-XII were as follows:

10 Catalyst Component A: As described in Example I  
containing 1.0% Cr, 0.6% P and 3.7% Al.

Catalyst Component B: As described in Example I  
containing 1.0% Cr.

15 Catalyst Component D: A commercially available  
chromium-containing catalyst (EP30 from Crosfield  
Catalysts - chromium acetate on silica having a pore  
volume of 1.6 cc/g) was additionally impregnated with  
boron. The boron was incorporated by adding  
trimethylborate to a slurry of chromium-containing  
20 catalyst in methylene chloride and evaporating the  
solvent. Chromium and boron contents were 1.0% and  
1.2%, respectively.

Catalyst Component E: Titanium was incorporated on  
the chromium-containing silica used for Catalyst  
25 Component D. Deposition was accomplished in the usual  
manner using tetrapropyltitanate and methylene  
chloride as the solvent. After drying, the catalyst  
component was analyzed and found to contain 1.0% Cr  
and 3.7% Ti.

30 Catalyst Component F: Silica (pore volume 2.3 cc/g)  
was calcined at 1650°F for 6 hours and impregnated  
with the reaction product of CrO<sub>3</sub> and triethyl

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1 phosphate. Titanium was then deposited utilizing the  
slurry technique with tetrapropyltitanate and  
5 methylene chloride. Analysis of the dried catalyst  
component showed it to contain 1.0% Cr, 0.69% P and  
3.7% Ti.

Catalyst Component G: A high pore volume silica (2.3  
cc/g) was calcined and chromium acetylacetonate  
deposited thereon. Titanium was then deposited as for  
10 Catalyst Component F to obtain a catalyst containing  
1.0% Cr and 3.7% Ti.

Catalyst Component H: The commercial chromium-  
containing catalyst employed for Catalyst Component D  
was additionally impregnated with aluminum using  
aluminum sec-butoxide and methylene chloride. The  
15 catalyst contained 1.0% Cr and 3.7% Al.

Catalyst Component I: The commercial chromium-  
containing catalyst employed for Catalyst Component D  
was modified with zirconium. The modification was  
accomplished by adding triisopropyl zirconate to a  
20 slurry of the chromium-containing catalyst in  
methylene chloride and evaporating the solvent.  
Chromium and zirconium contents were 1.0% and 3.7%,  
respectively.

Polymerizations for Examples V-XII were  
25 conducted in a one-liter autoclave equipped with a  
mechanical overhead stirrer and an external jacket for  
regulating temperature. The polymerization was  
performed by providing the continuous addition of  
ethylene at a fixed total pressure. The reactor had  
30 thermocouples to control the temperature of the  
external jacket and the internal temperature of the  
reactor during the polymerization. Ethylene fed to

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1 the reactor was passed through an electronic gas flow  
meter to permit continuous monitoring of the ethylene  
flow to the reactor. All handling of the  
polymerization reaction components was carried out  
5 using airless techniques to exclude oxygen and water.  
The polymerizations were conducted in a slurry of  
isobutane which had been dried and deoxygenated. The  
autoclave was charged first with catalyst and then  
with 450 ml isobutane. The autoclave was then heated  
10 and the introduction of ethylene was commenced when  
the desired temperature was reached.

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EXAMPLE V

5 A mixed catalyst was prepared by combining Catalyst Component A (high pore volume) and Catalyst Component D (low pore volume) at a weight ratio of 1:1. The mixture was then activated by fluidizing with dry air at 2 feet per minute lineal velocity and heating at 1200°F for 6 hours. The resulting mixed catalyst thus obtained was then evaluated for its ability to polymerize ethylene in accordance with the procedure described above. Two polymerizations, identified as Run A and Run B, were made and the conditions employed for each and results obtained were as follows:

	Run A	Run B
15 Temperature (°F)	221	221
Other Pzn Variables	8.5	8.5
Polymer Recovered (grams)	150	124
20 Productivity <sup>1</sup>	1194	2094
Activity <sup>2</sup>	3256	2417
Resin Properties:		
25 Density	.9554	N.D. <sup>3</sup>
MI	0.48	0.092
HLMI	35.9	11.5
MIR	74.8	124.6

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<sup>1</sup> Grams polymer per gram of catalyst<sup>2</sup> Grams polymer per gram of catalyst per hour<sup>3</sup> N.D. = not determined

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EXAMPLE VI

Three mixed catalysts were prepared by combining Catalyst Component A and Catalyst Component E at different weight ratios and used to polymerize ethylene. The mixed catalysts were activated at 1100°F for 6 hours in air. Compositions of the mixed catalysts, details of the polymerizations and properties of the resins produced were as follows:

	Run A	Run B	Run C
Wt. Ratio A:E	1:1	4:1	1:4
Temperature (°F)	221	221	221
Ethylene in Reactor (wt.%)	8.5	8.5	8.5
Polymer Recovered (grams)	72	142	131
Productivity	1283	2178	2060
Activity	1426	2513	2247
Resin Properties:			
Density	.9598	.9591	.9628
MI	.74	.19	1.14
HLMI	58.1	16.9	77.6
MIR	78.5	88.7	68.1



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EXAMPLE VII

A mixed catalyst containing chromium, phosphorus and titanium was prepared by combining Catalyst Component F and Catalyst Component B at a 1:1 wt. ratio. Two polymerizations were conducted using the mixed catalyst. For the first polymerization (Run A) the mixed catalyst was activated by heating in air at 1200°F for 6 hours and for the second polymerization (Run B) the catalyst was activated in air at 1100°F for six hours. Results were as follows:

	Run A	Run B
Temperature (°F)	221	221
Ethylene in Reactor (wt.%)	8.5	8.5
Polymer Recovered (grams)	138	135
Productivity	1618	2292
Activity	2489	2547
Resin Properties:		
Density	N.D.	.9548
MI	0.43	0.21
HLMI	36.8	16.3
MIR	85.6	77.7

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EXAMPLE VIII

Mixed catalysts containing chromium, titanium, and aluminum obtained by combining higher pore volume based Catalyst Component G with lower pore volume based Catalyst Component H were prepared, activated in air at 1100°F in the usual manner and evaluated for the polymerization of ethylene. Results were as follows:

	Run A	Run B
Wt. Ratio G:H	1:1	4:1
Temperature (°F)	221	221
Ethylene in Reactor (%)	8.5	8.5
Polymer Recovered (grams)	112	128
Productivity	2171	1960
Activity	2368	2330
Resin Properties:		
Density	.9595	.9606
MI	0.68	1.10
HLMI	46.1	77.0
MIR	67.8	70

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EXAMPLE IX

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Mixed catalysts containing chromium, titanium, and boron were obtained by combining Catalyst Component G with Catalyst Component D. The mixed catalysts were activated at 1200°F in the usual manner and used to polymerize ethylene. Results were as follows:

		Run A	Run B
10	Wt. Ratio G:D	2:1	1:1
	Temperature (°F)	221	221
	Ethylene in Reactor (%)	8.5	8.5
	Polymer Recovered (grams)	132	114
15	Productivity	1803	1344
	Activity	3381	1753
	Resin Properties:		
20	Density	N.D.	.9585
	MI	1.0	1.25
	HLMI	58.1	90.9
	MIR	58.1	72.7

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EXAMPLE X

1 To further demonstrate the versatility of  
the invention and the ability to vary resin properties  
by changing the activation conditions, the following  
5 experiment was conducted. For this example the mixed  
catalyst of Example VI, comprised of a mixture of one  
part Catalyst Component A (chromium, aluminum and  
phosphorous on higher pore volume silica) and one part  
Catalyst Component E (chromium and boron on lower pore  
10 volume silica), was activated utilizing a multiple  
step procedure. The activation procedure entailed:  
(a) heating the mixed catalyst to approximately 300°F  
under nitrogen over a one hour period; (b) maintaining  
the mixed catalyst at 300°F for two hours under  
15 nitrogen; (c) gradually increasing the temperature of  
the mixed catalyst to 1290°F over a 6 hour period  
under an atmosphere of carbon monoxide and nitrogen  
(wt. ratio 3:97); (d) maintaining the mixed catalyst  
at 1290°F for 6 hours under the CO/N<sub>2</sub> atmosphere; (e)  
20 cooling the mixed catalyst to 930°F over a 2 hour  
period under nitrogen; (f) heating the mixed catalyst  
for one hour in air at 930°F; and (g) cooling the  
mixed catalyst to ambient temperature over a period of  
5 hours under nitrogen. The total time required for  
25 this activation procedure was 23 hours.

The mixed catalyst activated in the above  
manner was employed for the polymerization of  
ethylene. Polymerization conditions and properties of  
the resulting resin were as follows:

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1		Run A	Run B
	Temperature (°F)	214	201
5	Ethylene in Reactor (%)	5	5
	Polymer Recovered (grams)	93	119
	Productivity	1970	1653
	Activity	1970	1417
10	Resin Properties:		
	Density	.9619	.9625
	MI	0.52	0.08
	HLMI	45.8	11.8
15	MIR	88	147.5

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EXAMPLE XI

Utilizing the activation procedure of Example X, a mixed catalyst obtained by combining two parts Catalyst Component A with one part Catalyst Component E was prepared and used to polymerize ethylene. Results were as follows:

Temperature (°F) 212

Ethylene in Reactor (%) 5

Polymer Recovered (grams)

Productivity 1918

Activity 2131

Resin Properties:

Density .9604

MI 0.105

HLMI 17.8

MIR 169.5

EXAMPLE XII

1 A mixed catalyst containing chromium,  
aluminum, phosphorus and zirconium was prepared by  
combining Catalyst Component A and Catalyst Component  
5 I at a 1:1 ratio. The mixed catalyst was then  
activated following the procedure of Example X and  
employed for the polymerization of ethylene.  
Polymerization conditions employed and resin  
properties were as follows:

10	Temperature (°F)	212
	Ethylene in Reactor (%)	5
	Polymer Recovered (grams)	102
	Productivity	1977
	Activity	2118
15	Resin Properties:	
	Density	.9603
	MI	0.02
	HLMI	7.5
	MIR	375

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1 We claim:

5 1. A mixed chromium catalyst composition containing a first and second silica-supported chromium catalyst component; said first and second catalyst components present at a weight ratio from 10:1 to 1:10 and each containing from 0.1 to 2.0 weight percent chromium with at least one of said catalyst components containing an additional metallic or non-metallic element selected from aluminum, 10 titanium, zirconium, boron or phosphorus with the proviso that when one of the catalytic components contains chromium and aluminum the other component shall contain more than one metallic or non-metallic catalytic element; and the silica supports of said 15 first and second catalyst components differing in pore volume by at least 0.3 cc/g.

20 2. The mixed chromium catalyst composition of Claim 1 wherein prior to thermal activation in the non-reducing atmosphere the first catalyst component, the second catalyst component or a mixture of the first and second catalyst components is heated in a reducing atmosphere at 575°F to 1650°F.

25 3. The mixed chromium catalyst composition of Claim 2 wherein the reducing atmosphere is a mixture of nitrogen and carbon monoxide.

30 4. The mixed chromium catalyst composition of Claim 1, 2 or 3 wherein the weight ratio of the first and second catalyst components is from 5:1 to 1:5 and the pore volume of the silica support of the first catalyst component is greater than 1.0 cc/g and at least 0.3 cc/g higher than the pore volume of the silica support of the second catalyst component.

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1           5. The mixed chromium catalyst composition  
of Claim 4 wherein the pore volume of the silica  
support of the first catalyst component is from 1.7 to  
3.1 cc/g and the pore volume of the silica support of  
5       the second catalyst component is from 1.0 to 2.0 cc/g.

6. The mixed chromium catalyst composition  
of any of Claims 1 to 5 wherein either or both of the  
silica supports employed for the first and second  
catalyst components is calcined at a temperature from  
10       200°F to 1800°F prior to metal deposition.

7. The mixed chromium catalyst composition  
of Claim 3 wherein the metallic or non-metallic  
element is present in an amount from 0.1 to 6.0 weight  
percent and the first catalyst component, the second  
15       catalyst component or a mixture of the first and  
second catalyst components is thermally activated by  
heating in a non-reducing atmosphere at a temperature  
from 450°F to 1700°F.

8. The mixed chromium catalyst composition  
20       of any of Claims 1 to 7 wherein the first catalyst  
component contains 0.5 to 1.2 weight percent chromium,  
14.5 weight percent aluminum and 0.1 to 1.0 weight  
percent phosphorus and the second catalyst component  
contains 0.75 to 1.25 weight percent chromium.

9. The mixed chromium catalyst composition  
25       of Claim 8 wherein 2 to 4.5 weight percent titanium or  
zirconium is additionally present.

10. The mixed chromium catalyst composition  
of Claim 9 wherein the titanium is associated with the  
30       first catalyst component.

1           11. The mixed chromium catalyst composition  
of any of Claims 1 to 10 wherein a metallic or non-  
metallic reducing agent is present and the molar ratio  
of the metal or non-metal of said reducing agent to  
chromium ranges from 0.01:1 to 5:1.

5           12. The mixed chromium catalyst composition  
of Claim 9 wherein the metallic or non-metallic  
reducing agent is selected from the group consisting  
of trialkyl aluminums, alkyl aluminum halides, alkyl  
10   aluminum alkoxides, dialkyl zincs, dialkyl magnesiums,  
alkali metal borohydrides, aluminum borohydrides,  
alkyl boranes, and boron hydrides.

15           13. The mixed chromium catalyst composition  
of Claim 12 wherein the reducing agent is triethyl  
borane.

20           14. In a process for the particle form  
polymerization of ethylene, to produce high density  
resins useful for blow molding with broadened  
molecular weight distributions, the improvement  
comprising conducting the polymerization in the  
presence of a mixed catalyst set forth in any of  
Claims 1 to 13.

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# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/02337

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC (5): C08F 4/648, C08F 4/69, C08F 4/646		
US CL : 502/113; 526/106		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
U.S.	502/113, 117, 120, 162, 204, 210, 242; 526/105, 106	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category*	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
A	US, A, 3,622,521 (HOGAN ET AL.) 23 November 1971, See Abstract, col. 1, lines 8-28 & the examples.	1-14
A	US, A, 3,984,351 (REKERS ET AL.) 05 October 1976, See Abstract, col 2, lines 1-19 & the examples.	1-8, 11, 14
A	US, A, 3,985,676 (REKERS ET AL.) 12 October 1976, See Abstract col. 2, line 60 to col. 3, line 17 & the examples.	1-8, 11, 14
A	US, A, 4,263,422 (LOWERY ET AL.) 21 April 1981, See Abstract, col. 1, lines 31-41 & the examples.	1-14
A	US, A, 4,295,997 (McDANIEL ET AL.) 20 October 1981, See Abstract, col., line 54 to col. 2, line 10 & the examples.	1-8, 11, 14
A	US, A, 4,454,242 (IKEGAMI ET AL.) 12 June 1984, See Abstract, col. 1, line 57 to col. 2, line 10 & the examples.	1-14
A	US, A, 4,540,757 (McDANIEL) 10 September 1985, See Abstract, col. 2, lines 5-18 & the examples.	1-14
<p>* Special categories of cited documents:<sup>15</sup></p> <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>2</sup>		Date of Mailing of this International Search Report <sup>2</sup>
30 JUNE 1992		14 JUL 1992
International Searching Authority <sup>1</sup>		Signature of Authorized Officer <sup>20</sup>
ISA/US		<i>Patrick P. Garvin</i> PATRICK P. GARVIN

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US, A, 4,560,733 (MARTIN ET AL.) 24 December 1985, See Abstract, col. 2, lines 1-14 & the examples.	1-14
A,P	US, A, 5,081,089 (REKERS ET AL.) 14 January 1992, See Abstract, col. 2, lines 43-66.	1-8,11,14

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

1. ☐ Claim numbers \_\_, because they relate to subject matter (1) not required to be searched by this Authority, namely:
2. ☐ Claim numbers \_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out (1), specifically:
3. ☐ Claim numbers \_\_, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Search Authority did not invite payment of any additional fee.

Remark on protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.